

1 **POLYALPHAOLEFINS WITH IMPROVED OXIDATIVE STABILITY**
2 **AND THE PROCESS OF MAKING THEREOF**

3 **CROSS-REFERENCE TO RELATED APPLICATIONS**

4 This application is a Continuation-In-Part of U.S. Application Serial
5 No. 09/108,048, filed June 30, 1998.

6 **FIELD OF THE INVENTION**

7 The present invention relates to oxidatively stable polyalphaolefins and
8 lubricating composition comprising same. More particularly, the present
9 invention relates to compositions of lubricants using synthetic
10 polyalphaolefins derived from 1-decene, 1-dodecene or 1-tetradecene olefins
11 which exhibit improved oxidative stability.

12 **BACKGROUND OF THE INVENTION**

13 Lubricants today are being called upon to work in ever more demanding
14 applications. In many applications, greater thermal and oxidative
15 performance are necessary to meet rigorous requirements. For instance,
16 today's automobiles tend to have smaller, more demanding engines that
17 operate at higher temperatures. Thus, the engine oil has to function in an
18 increasingly severe environment while meeting fuel economy demands.
19 Besides changes in the additive package, increasingly synthetic base oils are
20 being used instead of conventional mineral oils. Of the synthetic oils,
21 polyalphaolefins (PAO) are among the most popular.

22 PAO is manufactured by oligomerization of linear alpha olefin followed by
23 hydrogenation to remove unsaturated moieties and fractionation to obtain the
24 desired product slate. 1-decene is the most commonly used alpha olefin in

1 the manufacture of PAO, but 1-dodecene and 1-tetradecene can also be
2 used. PAO's are commonly categorized by the numbers denoting the
3 approximate viscosity in centistokes of the PAO at 100°C. It is known that
4 PAO 2, PAO 2.5, PAO 4, PAO 5, PAO 6, PAO 7, PAO 8, PAO 9 and PAO 10
5 and combinations thereof can be used in engine oils, gear oils, compressor
6 lubricants, hydraulic fluids and a variety of other applications. The most
7 common of these are PAO 4, PAO 6 and PAO 8.

8 It has long been known that hydrogenation to achieve a PAO which is
9 predominantly saturated achieves a more desirable product, one that is more
10 stable to oxidation and heat.

11 Several patents disclose processes for hydrogenating PAO's. These include
12 the following:

13 Jackson et al. (U.S. Patent No. 4,125,569) discloses a process for
14 hydrogenating polymerized olefins in the presence of alumina and a
15 hydrogenated catalyst to provide a greater hydrogenation rate than what is
16 obtained using the catalyst alone.

17 Petrillo et al. (U.S. Patent No. 4,167,534) discloses the possibility of generally
18 improving stability to both oxidation and heat as well as specifically improving
19 viscosity index and pour point by including a hydrogenation step to eliminate
20 unsaturations in the process of synthesizing lubricating oils from an n-olefin
21 cut. It does not give any data supporting its general assumption that
22 oxidative stability of the lubricant is improved by decreasing unsaturation.

23 Degnan et al. (U.S. Patent No. 5,573,657) discloses hydrogenating lubricants
24 using a catalyst based on an ultra-large-pore crystalline material.

1 With today's automobiles, engine oils and lubricants with high oxidative
2 stability are needed. Various tests to measure oxidative stability are known.
3 These include the Lube Oil Oxidator test, the Rotary Bomb Oxidation Test
4 (RBOT), and the Penn State Microoxidation Test among others. Using such
5 tests, attempts have been made to correlate increased oxidative stability with
6 other components or factors in the oil or lubricant.

7 Ripple and Fuhrmann in "Performance Comparisons of Synthetic and Mineral
8 Oil Crankcase Lubricant Base Stocks" (*Journal of Synthetic Lubricants*, 6-3,
9 pp. 209-232, 1989) state that engine oil formulations using synthetic (PAO)
10 base oils provide for superior performance to mineral oils in bench and engine
11 testing as well as field service testing. This is due to the fluid's increased
12 oxidative stability, reduced oil consumption, cleaner engines and longer drain
13 capabilities. Specifically, the oxidative stability is supported by reduced
14 viscosity increase. But there is nothing in the paper, which attributes this
15 increase to any specific physical property such as decreased unsaturation as
16 measured by Bromine Index.

17 Gunsel et al. in "Evaluation of Some Poly-Alpha-Olefins in a Pressurized
18 Penn State Microoxidation Test" (*Journal of the Society of Tribologists and*
Lubrication Engineers, 43, 8, pp. 629-635, 1987) compared two PAO's, one
20 with a stated Bromine Index of 1323 and the other with a stated Bromine
21 Index of two. With a Penn State Microoxidation test with two additive
22 packages, phenyl alpha naphthylamine (PAN) and zinc dialkyl dithio
23 phosphate (ZDDP), side by side results of 1% PAN and 1.88% ZDDP/0.5%
24 PAN show that there may be some slight improvement in oxidative stability for
25 PAO having extremely low Bromine Index over PAO having a relatively high
26 Bromine Index, but the advantage does not appear significant since there is
27 so much scatter in the data that there ends up being no difference
28 statistically.

1 Even though teachings in the art generally support the presumption that a
2 decrease in unsaturation in the PAO contained in PAO based lubricants will
3 have some improving effect on oxidation stability, when such an effect was
4 actually tested by Gunsel et al., the effect was found to be slight. Therefore,
5 the art is devoid of the significant benefit realized by greatly hydrogenating
6 PAO's to increase oxygen stability in PAO based lubricants.

7 SUMMARY OF THE INVENTION

8 The present invention relates to a highly oxidative stable polyalphaolefin
9 method of producing a highly oxidatively stable polyalphaolefin comprising the
10 step of hydrogenating a polyalphaolefin to a level of hydrogenation in which a
11 Bromine Index of less than 200 mg Bromine per 100 gram sample of
12 polyalphaolefin is achieved. In more preferred embodiments, the present
13 invention relates to the above method in which a Bromine Index of less than
14 100 mg Bromine per 100 gram sample of polyalphaolefin is achieved, a
15 Bromine Index of less than 50 mg Bromine per 100 gram sample of
16 polyalphaolefin is achieved, and a Bromine Index of less than 25 mg Bromine
17 per 100 gram sample of polyalphaolefin is achieved.

18 In another embodiment, the present invention relates to a lubricating
19 composition comprised of the highly oxidative stable polyalphaolefin. The
20 present invention, and the benefits realized in its practice, is based at least in
21 part on the recognition that by going to near complete hydrogenation, one
22 achieves a surprising improvement in oxidative stability for polyalphaolefins.

23 DESCRIPTION OF THE FIGURE

24 The Figure of the Drawing plots the results of experiments showing oxidation
25 over time in a Penn State Microoxidation Test of two PAO's (a typical
26 moderately hydrogenated PAO and a highly saturated product) along with

1 results given in Gunsel et al. The GPC data, which has been analyzed by the
2 inventors, has been modified to fit the scale of Figure 2 in Gunsel et al.

3 DETAILED DESCRIPTION OF THE INVENTION

4 Investigators continue to search for ways to increase oxidation stability in
5 PAO's. The inventors in the present application have found a surprising
6 increase in oxidative stability as a result of hydrogenating PAO's to decrease
7 unsaturation to a Bromine Index below 200. The Bromine Index (ASTM
8 D 2710) is the number of milligrams of Bromine that react with 100 grams of
9 sample under the conditions of the test. In contrast, the Bromine Number
10 method (ASTM D 1159), as mentioned in Petrillo et al. (U.S. Patent
11 No. 4,167,534) is the number of grams that react with 100 grams of sample
12 under the conditions of the test. Therefore, there is a natural factor of 1000
13 difference between the two methods. This increase in oxidative stability is
14 measured with both Rotary Bomb Oxidation Test (RBOT) (ASTM D 2272) and
15 Lube Oil Oxidator tests. The degree of increase of oxidative stability
16 conferred by the hydrogenation step is far beyond what would be expected
17 from previous teachings in the art.

18 The Bromine Index method, ASTM D 2710, was developed to determine the
19 degree of unsaturation in petroleum hydrocarbons, such as cumenes,
20 reformates and kerosenes. Nevertheless, it has historically been utilized as a
21 measure for the degree of unsaturation for PAO's. The chemical structure of
22 PAO differs from the aforementioned petroleum hydrocarbons in terms of the
23 degree of branching and therefore there is a greater steric hindrance to the
24 bromination reaction for PAO. In addition, PAO is limited in solubility in the
25 test solvent, which creates problems with accuracy and repeatability.
26 Therefore, the Bromine Index method has been modified from the original
27 ASTM D 2710 specifically for PAO and is designated as K801.

1 The present inventors have found specific modifications useful in increasing
2 the accuracy and repeatability and decreasing the level of detection for PAO
3 measurements. The modifications have been to utilize isopropanol as an
4 additional solvent and operate at higher temperatures to aid solubility as well
5 as take blank measurements for each titration solvent. In addition, the
6 present inventors have also identified that it is preferred to utilize a specific
7 instrument vendor (Mettler) for the Bromine Index apparatus. This has
8 resulted in improvements in both accuracy and repeatability based upon
9 measurement standards for PAO.

10 The present inventors used the above modifications to the original Bromine
11 Index method to more accurately determine Bromine Index of a moderately
12 hydrogenated PAO product and a highly saturated product and then
13 determined oxidative stability of these products using the Penn State
14 Microoxidation method under the same equipment and under the same
15 conditions as in Gunsel et al.'s Figure 2, as described in Example 11
16 hereafter. The present inventors found that the oxidative stability of both a
17 moderately hydrogenated PAO product (having a Bromine Index of 433
18 measured with the modified method) and a highly saturated PAO product
19 (with a Bromine Index of 0.95 measured with the modified method) was
20 significantly better than the oxidative stability of Gunsel et al.'s Fluid B (a PAO
21 fluid having a stated Bromine Index of 2 measured by the unmodified Bromine
22 Index method). Thus, Gunsel et al.'s hydrogenated PAO (Fluid 2) was not
23 nearly as oxidatively stable as either a typical hydrogenated PAO product with a Bromine
24 Index of 433 or a highly saturated PAO product with a Bromine
25 Index of 0.95 in accordance with the present invention, as measured by the
26 improved Bromine Index measurement methods.

27 The present inventors have also found that when they hydrogenate the PAO
28 twice, both before and after a distillation step, they achieve a better result in

- 1 both the RBOT and Lube Oil Oxidator tests than they do when only one
- 2 hydrogenation step is performed with a distillation step.
- 3 In its broadest aspect, the present invention involves improving thermal
- 4 oxidative stability by hydrogenating PAO's especially those derived from
- 5 1-decene, 1-dodecene or 1-tetradecene as a base oil. The level of
- 6 hydrogenation preferably approaches the removal of all unsaturation, but is at
- 7 least to a level such that the Bromine Index is less than 200 mg Bromine per
- 8 100 gram of polyalphaolefin.
- 9 The PAO's described in the present invention can be used, as in the following
- 10 non-limiting examples, as engine oil lubricant, gear lubricant, hydraulic
- 11 lubricant, compressor lubricant, aerospace jet lubricant, fiber optic cable gel,
- 12 synthetic grease, and dielectric fluid.
- 13 The present invention also relates to a method of producing a highly
- 14 oxidatively stable polyalphaolefin comprising the step of hydrogenating
- 15 polyalphaolefin to a level of hydrogenation in which an RBOT level of at least
- 16 2200 minutes is achieved when diphenyl amine is used as an antioxidant.
- 17 This is illustrated in Examples 1-8.
- 18 The present invention also relates to a method of producing a highly
- 19 oxidatively stable polyalphaolefin comprising the step of hydrogenating
- 20 polyalphaolefin to a level of hydrogenation in which a Lube Oil Oxidator level
- 21 of at least 45 hours is achieved when pressures between 100 and 2500 psi
- 22 are applied. This is illustrated in Examples 9 and 10.
- 23 The present invention also relates to a method comprising distilling the
- 24 polyalphaolefin to remove impurities, then hydrogenating the polyalphaolefin
- 25 to achieve a final polyalphaolefin product having a Bromine Index of less than

1 200 mg Bromine per 100 gram sample of polyalphaolefin. This is illustrated in
2 Example 9.

3 The present invention also relates to a method comprising a preliminary step
4 of hydrogenating the polyalphaolefin followed by distilling to remove
5 impurities, followed by a hydrogenating step to achieve a final polyalphaolefin
6 product having a Bromine Index of less than 200 mg Bromine per 100 gram
7 sample of polyalphaolefin. This is illustrated in Example 10, and is a
8 preferred embodiment of the present invention.

9 ADDITIVE COMPONENTS

10 The following additive components are examples of some components that
11 can be favorably employed in the preparation of the lubricating composition in
12 accordance with the present invention. These examples of additives are
13 provided to illustrate the present invention, but they are not intended to limit it:

14 (1) Metal detergents: sulfurized or unsulfurized alkyl or alkenyl phenates,
15 alkyl or alkenyl aromatic sulfonates, sulfurized or unsulfurized metal
16 salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or
17 alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or
18 alkenyl naphthenates, metal salts of alkanoic acids, metal salts of an
19 alkyl or alkenyl multi-acid, metal salts of an alkyl salicylic acid,
20 carboxylates, overbased detergents and chemical and physical mixtures
21 thereof.

22 (2) Ashless dispersants: alkenyl succinimides, alkenyl succinimides
23 modified with other organic compounds, and alkenyl succinimides
24 modified with boric acid, alkenyl succinic ester.

1 (3) Oxidation inhibitors:

- 2 (a) Phenol type oxidation inhibitors: 4,4'-methylenebis (2,6-di-tert-
3 butylphenol), 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-
4 tert-butylphenol), 2,2'-(methylene bis (4-methyl-6-tert-butyl-phenol),
5 4,4'-butyldenebis(3-methyl-6-tert-butylphenol),
6 4,4'-isopropylidenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-
7 methyl-6-nonylphenol), 2,2'-isobutylidene-bis(4,6-dimethylphenol),
8 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-
9 4-methyl-phenol, 2,6-di-tert-butyl-4-ethylphenol, 2,4-dimethyl-6-
10 tert-butyl-phenol, 2,6-di-tert-4-(N,N' dimethylaminomethylphenol),
11 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-
12 tert-butylphenol), bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)-
13 sulfide, and bis (3,5-di-tert-butyl-4-hydroxybenzyl).

14 (b) Diphenylamine type oxidation inhibitor: alkylated diphenylamine,
15 phenyl-I-naphthylamine, and alkylated I-naphthylamine.

16 (c) Other types: metal dithiocarbamate (e.g., zinc dithiocarbamate),
17 and methylene bis (dibutyl dithio carbamate).

18 (4) Rust inhibitors (Anti-rust agents):

- 19 (a) Nonionic polyoxyethylene surface active agents: polyoxyethylene
20 lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene
21 nonylphenyl ether, polyoxyethylene octylphenyl ether,
22 polyoxyethylene octyl stearyl ether, polyoxyethylene oleyl ether,
23 polyoxyethylene sorbitol monostearate, polyoxyethylene sorbitol
24 mono-oleate, and polyethylene glycol monooleate.

- 1 (b) Other compounds: stearic acid and other fatty acids, dicarboxylic
2 acids, metal soaps, fatty acid amine salts, metal salts of heavy
3 sulfonic acid, partial carboxylic acid ester of polyhydric alcohol, and
4 phosphoric ester.
- 5 (5) Demulsifiers: addition product of alkylphenol and ethylene oxide,
6 polyoxyethylene alkyl ether, and polyoxyethylene sorbitan ester.
- 7 (6) Extreme pressure agents (EP agents): zinc dithiophosphates, zinc
8 dithiocarbamates, zinc dialkyl dithiophosphate (primary alkyl type &
9 secondary alkyl type), zinc diaryl dithiophosphate, sulfurized oils,
10 diphenyl sulfide, methyl trichlorostearate, chlorinated naphthalene,
11 fluoroalkylpolysiloxane, and lead naphthenate.
- 12 (7) Friction modifiers: fatty alcohol, fatty acid, amine, borated ester, and
13 other esters.
- 14 (8) Multifunctional additives: sulfurized oxymolybdenum dithiocarbamate,
15 sulfurized oxymolybdenum organo phosphoro dithioate,
16 oxymolybdenum monoglyceride, oxymolybdenum diethylate amide,
17 amine-molybdenum complex compound, and sulfur-containing
18 molybdenum complex compound.
- 19 (9) Viscosity index improvers: polymethacrylate type polymers, ethylene-
20 propylene copolymers, styrene-isoprene copolymers, hydrated styrene-
21 isoprene copolymers, polyisobutylene, and dispersant type viscosity
22 index improvers.
- 23 (10) Pour point depressants: polymethyl methacrylate.

1 (11) Foam Inhibitors: alkyl methacrylate polymers and dimethyl silicone
2 polymers.

3 In one embodiment, an engine lubricating oil composition would contain:

4 (a) a major part of a base oil of lubricating viscosity, wherein the base oil
5 comprises 1-dodecene and/or 1-tetradecene-derived polyalphaolefins;

6 (b) 0% to 20% of at least one ashless dispersant;

7 (c) 0% to 30% of the detergent;

8 (d) 0% to 5% of at least one zinc dithiophosphate;

9 (e) 0% to 10% of at least one oxidation inhibitor;

10 (f) 0% to 1% of at least one foam inhibitor; and

11 (g) 0% to 20% of at least one viscosity index improver.

12 In a further embodiment, an engine lubricating oil composition is produced by
13 blending a mixture of the above components. The lubricating oil composition
14 produced by that method might have a slightly different composition than the
15 initial mixture, because the components may interact. The components can
16 be blended in any order and can be blended as combinations of components.

17 ADDITIVE CONCENTRATES

18 The use of additive concentrates is also included within the scope of this
19 invention. The concentrates of this invention comprise the compounds or
20 compound mixtures of the present invention, with at least one of the additives

1 disclosed above. Typically, the concentrates contain sufficient organic diluent
2 to make them easy to handle during shipping and storage.

3 From 20% to 80% of the concentrate is organic diluent. Suitable organic
4 diluents which can be used include for example, solvent refined 100N, i.e.,
5 Cit-Con 100N, and hydrotreated 100N, i.e., RLOP 100N, and the like. The
6 organic diluent preferably has a viscosity of from about 1 to about 20 cSt at
7 100°C.

EXAMPLES

9 The invention will be further illustrated by following examples, which set forth
10 particularly advantageous method embodiments. While the Examples are
11 provided to illustrate the present invention, they are not intended to limit it.

12 Examples 1 through 4 are comparative examples, which show typical
13 oxidative stability results for the described materials. Examples 5 through 8
14 are intended to show the advantages of the present invention.

Example 1

16 A commercial sample of Chevron 4 cSt polyalphaolefin Synfluid® obtained
17 and subjected to RBOT (ASTM D 2272), the aforementioned modified
18 Bromine Index and Lube Oil Oxidator measurements. The Lube Oil Oxidator
19 measurement is an oxygen uptake test wherein the amount of time is
20 measured until one liter of oxygen is consumed by the sample under the
21 conditions of the test. Under the conditions of the test, the sample is
22 formulated with an oxidation catalyst to promote oxidation and an antioxidant
23 at a controlled temperature and pressure. The RBOT test is an oxygen
24 uptake test, which monitors pressure changes in a sample bomb at elevated

1 temperature and pressure in the presence of a copper oxidation catalyst. The
2 results are shown in Table 1.

3 TABLE 1

4

Example	PAO Grade	RBOT*, min	Lube Oil Oxidator, hrs	Bromine Index
1	4	1267	16	682
2	6	826	16	433
3	5	1883	27	172
4	7	1918	25	108
5	4	2214	48	2.6
6	6	1905	>50	1.6
7	5	2233	57	10
8	7	2217	44	5

5

6 *All of the samples for RBOT were formulated with 0.5 weight percent of
7 Uniroyal's Naugalube® 640 antioxidant.

8

9

Example 2

10 The procedure of Example 1 was repeated except 6 cSt polyalphaolefin was
11 utilized instead of 4 cSt polyalphaolefin. The results are shown in Table 1.

12

Example 3

13 The procedure of Example 1 was repeated except 5 cSt polyalphaolefin was
14 utilized instead of 4 cSt polyalphaolefin. The results are shown in Table 1.

15

Example 4

16 The procedure of Example 1 was repeated except 7 cSt polyalphaolefin was
17 utilized instead of 4 cSt polyalphaolefin. The results are shown in Table 1.

1

Example 5

2 A sample of Chevron 4 cSt polyalphaolefin Synfluid® was subjected to an
3 additional hydrogenation step at 1500 psig. The resultant material was
4 subjected to RBOT (ASTM D 2272), the aforementioned modified Bromine
5 Index and Lube Oil Oxidator measurements. The Lube Oil Oxidator
6 measurement is an oxygen uptake test wherein the amount of time is
7 measured until one liter of oxygen is consumed by the sample under the
8 conditions of the test. The results are shown in Table 1.

9

Example 6

10 The procedure of Example 5 was repeated except 6 cSt polyalphaolefin was
11 utilized instead of 4 cSt polyalphaolefin. The results are shown in Table 1.

12

Example 7

13 The procedure of Example 5 was repeated except 5 cSt polyalphaolefin was
14 utilized instead of 4 cSt polyalphaolefin and the hydrogenation pressure was
15 1000 psig of hydrogen. The results are shown in Table 1.

16

Example 8

17 The procedure of Example 5 was repeated except 7 cSt polyalphaolefin was
18 utilized instead of 4 cSt polyalphaolefin. The results are shown in Table 1.

19

Example 9

20 A crude polyalphaolefin was taken prior to hydrogenation. The material was
21 subjected to distillation to provide 4 cSt and 6 cSt viscosity products at 100°C,
22 then hydrogenated at 1000 psig. The material was the tested by the Lube Oil

1 Oxidator method. The results are shown in Table 2. The 4 cSt fluid is listed
2 as Example 9a and the 6 cSt fluid is listed as Example 9b.

3 Example 10

4 The procedure of Example 9 was repeated except an additional
5 hydrogenation step was carried out prior to the distillation step. The material
6 was tested by the Lube Oil Oxidator method. The results are shown in
7 Table 2. The 4 cSt fluid is listed as Example 10a and the 6 cSt fluid is listed
8 as Example 10b.

9 TABLE 2

Example	Lube Oil Oxidator, hrs
9a	46
9b	42
10a	30
10b	30

10 Example 11

11 Experiments were performed using the Penn State Microoxidation test
12 methods described in Gunsel et al. to compare oxidation over time of typical
13 moderately hydrogenated PAO (Bromine Index is 433) and highly saturated
14 PAO product (Bromine Index is 0.95) with the data described in Gunsel et al.
15 with regard to Fluid B (stated Bromine Index = 2). The results are plotted in
16 the Figure and show that compared to the results of Fluid B of Gunsel et al.,
17 there is substantially less formation of high molecular weight product for either
18 the typical moderately hydrogenated PAO or the highly saturated PAO in a
19 Penn State Microoxidation test for PAO's containing 1% phenyl alpha
20 naphthyl amine (PAN). The Microoxidation test was performed in the
21

- 1 identical equipment used by Gunsel et al. at Pennsylvania State University.
- 2 The test procedure was performed at 225°C and at atmospheric pressure as
- 3 described in Figure 2 of Gunsel et al. The GPC analysis was performed
- 4 under the same conditions as in Gunsel et al.
- 5 These results definitively show that the PAO described in Gunsel et al. as
- 6 having a Bromine Index of 2 is a material which lacks the oxidative stability of
- 7 the PAO of the present invention. In fact, the PAO described in Gunsel et al.
- 8 exhibits less oxidative stability than the moderately hydrogenated PAO
- 9 (Bromine Index = 433). The effect of saturation of PAO's on oxidative stability
- 10 is significantly and unexpectedly greater than what is taught in Gunsel et al..
- 11 This also shows that the Bromine Index of 2 in Fluid B reported by Gunsel
- 12 et al. is incorrect when specifically tested using modifications of the Bromine
- 13 Index method which resolve limitations in the capability of measuring low
- 14 Bromine Indices.
- 15 While the present invention has been described with reference to specific
- 16 embodiments, this application is intended to cover those various changes and
- 17 substitutions that may be made by those skilled in the art without departing
- 18 from the spirit and scope of the appended claims.